

# Rate Constants for the Reactions of Hydroxyl Radical with Several Alkanes, Cycloalkanes, and Dimethyl Ether

W. B. DeMore\* and K. D. Bayes

*Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109*

## Abstract

Relative rate experiments were used to measure rate constants and temperature dependencies of the reactions of OH with propane, n-butane, n-pentane, n-hexane, cyclopropane, cyclobutane, cyclopentane, cyclohexane, and dimethyl ether. To assure internal consistency, ratios were measured for seventeen reactant pairs among these reactants. All of the derived rate constants are based on an absolute rate constant of the OH + C<sub>2</sub>H<sub>6</sub> reaction using the Atkinson recommendation,  $k = 1.0\text{E-}11 \exp(-1094/T)$  cm<sup>3</sup>/molec-s. The rate constants obtained are as follows:

Propane:	$1.29\text{E-}11 \exp(-730/T)$	$k(298\text{K}) = 1.11\text{E-}12$
n-Butane:	$1.71\text{E-}11 \exp(-590/T)$	$k(298\text{K}) = 2.36\text{E-}12$
n-Pentane:	$2.07\text{E-}11 \exp(-515/T)$	$k(298\text{K}) = 3.67\text{E-}12$
n-Hexane:	$2.39\text{E-}11 \exp(-462/T)$	$k(298\text{K}) = 5.08\text{E-}12$
Cyclopropane:	$5.15\text{E-}12 \exp(-1254/T)$	$k(298\text{K}) = 7.65\text{E-}14$
Cyclobutane:	$1.62\text{E-}12 \exp(-611/T)$	$k(298\text{K}) = 2.09\text{E-}12$
Cyclopentane:	$2.57\text{E-}11 \exp(-501/T)$	$k(298\text{K}) = 4.79\text{E-}12$
Cyclohexane:	$3.71\text{E-}11 \exp(-511/T)$	$k(298\text{K}) = 6.68\text{E-}12$
Dimethyl ether:	$1.44\text{E-}11 \exp(-481/T)$	$k(298\text{K}) = 2.88\text{E-}12$

These results are compared with previous literature data and are discussed in terms of trends in pre-exponential factors and activation energies.

## Introduction

Reactions of OH with simple alkanes and cycloalkanes are among the most fundamental processes in chemical kinetics, especially as applied to atmospheric and combustion chemistry. Recent publications suggest that rate constant data for these reactions are for the most part well-known.<sup>10,23,16</sup> Nevertheless, trends in parameters such as Arrhenius activation energies and pre-exponential factors are not well-established, and in a few cases, such as cyclopropane and cyclohexane, there are serious discrepancies in the literature reports for the rates.

In the present work we have conducted a number of temperature-dependent relative rate measurements among ethane, propane, n-butane, n-pentane, n-hexane, cyclopropane, cyclopentane, and cyclohexane. The precision of this technique provides a clearer picture of the rate constant trends among these reactants, and offers some improvement in the reliability of the rate constant data. Dimethyl ether was included because of its intrinsic importance and because it serves as a convenient reference reaction for intercomparison of the alkanes.

## Methods

*Relative Rate Measurements.* The technique used in this work has been described in several recent publications.<sup>6,14,13</sup> The method involves measurement of the fractional loss of the reactant compound, compared to a reference compound, in the presence of OH. The OH radicals are produced by direct photolysis of H<sub>2</sub>O at 185 nm, or, for those cases such as dimethyl ether which absorb at 185 nm, by 254 nm photolysis of O<sub>3</sub> ( $5\text{--}10 \times 10^{16} \text{ cm}^{-3}$ ) in the presence of water vapor ( $3\text{--}5 \times 10^{17} \text{ cm}^{-3}$ ). For experiments significantly below 273 K, the water vapor pressure is too low for the foregoing methods to be used. In those experiments, we photolyzed a mixture of N<sub>2</sub>O and H<sub>2</sub> at 185 nm.





Under the low temperature conditions, the  $\text{OH} + \text{H}_2$  reaction is sufficiently slow that not all the  $\text{OH}$  is consumed. For all measurements, small concentrations of  $\text{O}_2$  were maintained to remove  $\text{H}$ -atoms and alkyl radicals.

Measurements were made using the stopped-flow method, for which the rate constant ratio is given by the equation,

$$\frac{k_{\text{reactant}}}{k_{\text{reference}}} = \frac{\ln(\text{DF})_{\text{reactant}}}{\ln(\text{DF})_{\text{reference}}} \quad (3)$$

where the quantity  $\text{DF}$  is the depletion factor; i. e., the ratio of initial concentration to final concentration. In the present experiments the concentration measurements were made with an SRI 8610 or HP 5890 gas chromatograph, using a flame ionization detector.. Concentrations were measured by expanding the cell contents into a sample loop. A silica gel column was used for most of the measurements. At each temperature at which a rate constant ratio was measured, depletion factors were varied over a sufficient range to test for linearity in the plot of  $\ln(\text{DF})_{\text{reactant}}$  vs  $\ln(\text{DF})_{\text{reference}}$ , to verify adherence to Equation 3.

Temperatures were determined using a platinum resistance thermometer traceable to a NIST calibration.

All the relative rate constants were placed on an absolute basis by reference to ethane, taking the Atkinson recommendation<sup>2</sup> for the rate constant (fitted to a 2-parameter Arrhenius expression at 298 K):

$$k(\text{ethane}) = 1.00\text{E-}11 \exp(-1094/T) \text{ cm}^3/\text{molec-s.} \quad (4)$$

This recommendation is in excellent agreement with the data of Talukdar et al.<sup>23</sup> and Donahue et al.<sup>9</sup> For ethane rates at temperatures below 250 K, as in the calculation of propane rates from low-temperature ethane-propane ratio measurements, we used a three parameter expression as suggested by Talukdar et al. which also fits the Donahue et al data:

$$k(\text{ethane}) = 1.53\text{E-}17 T^2 \exp(-512/T) \text{ cm}^3/\text{molec-s.} \quad (5)$$

The relative rate method is usually not sensitive to impurities, but in any case either research grade or minimum 99% pure chemicals were used. Cyclobutane was prepared from cyclobutyl bromide (Sigma-Aldrich) via a Grignard reagent.<sup>5</sup>

## Results

Table 1 shows the results of the ratio measurements at different temperatures for the various reaction pairs. Rate constants calculated from these ratios are shown in Figures 1-9, which include data from other laboratories for comparison. Arrhenius fits to the data are given in Tables 2-4.

*Propane.* (Figure 1). As shown in the figure and in Table 2, our derived rate expression for propane is in excellent agreement with the absolute rate constants of Talukdar et al.<sup>23</sup> and Donahue et al.<sup>10,9</sup> At 298 K the agreement is within 3% or better. There are small differences in the Arrhenius parameters, which are related to the fact that at low temperatures the relative rate data show slightly lower propane rate constants (i. e., a more linear Arrhenius plot) than observed in the absolute measurements, as seen in Figure 1. This is true regardless of whether the linear (Equation 4) or  $T^a$  expression (Equation 5) is used for the reference ethane rate constant.

*n-Butane.* (Figure 2). As in the propane case, the derived rate constant for n-butane is in excellent agreement (4% or better at 298 K) with both the Talukdar et al. and Donahue et al. data.

*n-Pentane.* (Figure 3). Pentane was measured relative to both propane and butane, and the results are in good agreement. Curiously, however, our results are about 8% lower than those of Donahue et al.<sup>10</sup> and Talukdar et al.,<sup>23</sup> which are in good agreement with each other. We note that our pentane to butane ratio measurement at 298 K, 1.57, is in excellent agreement with the Atkinson et al.<sup>3</sup> value at 299 K of 1.60. Our ratio data are also in good agreement with the results of Harris and Kerr<sup>12</sup>. Further, pentane was used along with propane and butane as references for hexane and cyclohexane, and the results showed no discrepancy when using our derived rate for pentane. It appears therefore that the absolute measurements for pentane are slightly high.

*n*-Hexane. (Figure 4). Hexane was measured relative to propane, butane, and pentane, and as seen in the figure the results are in good agreement with each other and with the absolute data of Donahue et al.<sup>10</sup>.

Cyclopropane. (Figure 5). Cyclopropane was measured relative to ethane. The results are in fair agreement with the absolute data of Dobe et al.,<sup>8</sup> at high temperatures, but somewhat poorer agreement with data of Donahue et al.<sup>9</sup> and Jolly et al.<sup>15</sup>

Cyclobutane. (Figure 6). Our rate constants are in fair agreement (about 20% higher) than those of Dobe et al.<sup>8</sup> We tested for possible complications due to impurities that might not be resolved in the GC analysis of the cyclobutane sample by conducting experiments at very large conversions and also by (in one case) simultaneous IR analysis of cyclobutane via its strong C-H band near 2985 cm<sup>-1</sup>.<sup>17</sup> No evidence of significant impurity effects was found.

Cyclopentane. (Figure 7). Cyclopentane was measured relative to butane and hexane, and the results are in excellent agreement with each other and with the absolute data of Droege and Tully,<sup>11</sup> and Jolly et al.<sup>15</sup> A relative rate measurement by Atkinson et al.<sup>4</sup> at 299 K is in perfect agreement with our data. The absolute data of Donahue et al.<sup>10</sup> are slightly higher and show lower Arrhenius parameters (see Table 3).

Cyclohexane. (Figure 8). Cyclohexane was measured relative to propane, butane, and pentane, with excellent agreement among the results. Absolute data by Droege and Tully,<sup>11</sup> Saunders et al.,<sup>21</sup> and Donahue et al.<sup>9</sup> are in good agreement, although the absolute data tend to yield a slightly higher  $k(298\text{ K})$  (about 7%). Relative rate data by Sommerlade et al.<sup>22</sup> vs hexane are in excellent agreement with our data.

Dimethyl Ether. (Figure 9). Our relative rate measurements vs butane, pentane, and cyclohexane are in good agreement (7% or better). Among the absolute data, our results agree best with Tully and Droege<sup>24</sup>. Absolute data of Mellouki et al.,<sup>18</sup> Wallington et al.,<sup>25</sup> and Arif et al.<sup>1</sup> are in approximate agreement.

## Discussion

### *Rate Constants for the Alkanes, Cycloalkanes and Dimethyl ether.*

Our relative rate data, referenced ultimately to ethane using the Atkinson recommendation, have proven to be in good agreement among themselves and with recent absolute data. Cross-correlations among different reaction pairs tend to substantiate the accuracy of the data. The best agreement with absolute data was for propane, butane, hexane, cyclopentane, and cyclohexane. Poorest agreement was for pentane and cyclopropane. For dimethyl ether, the absolute data are in approximate agreement with our derived rate constant. We believe that all the rate constants reported here can be used with confidence with an uncertainty of about 5% at room temperature and with an uncertainty in the E/R values of the order of 100 K. The latter value comes mainly from uncertainty in the temperature dependence of the reference reaction, with some small additional uncertainty arising from error in the relative rate measurements

### *Reactivity of -CH<sub>2</sub>- Groups in n-Alkanes and Cycloalkanes.*

There are some striking similarities in the rate behavior of methylene groups in the n-alkanes and the cycloalkanes. These can be seen most clearly by removing the contribution of the CH<sub>3</sub> groups from the alkane rates. To do this we assume that the contribution is equal to the ethane rate, so that the net rate constant of the residual methylene groups is given by

$$k(\text{CH}_2)_n = (k_{\text{alkane}} - k_{\text{ethane}}) \quad (6)$$

We then do an Arrhenius plot of the net rate constants over the temperature range of the present experiments to determine the Arrhenius parameters. The resulting A-factor and E/R values are shown in Table 5. From this table it is seen that the rate constant per methylene group is slightly smaller in propane than in the higher alkanes. As discussed by Talukdar et al.,<sup>23</sup> this is due to the fact that the methylene environment in propane is not the same as in the higher alkanes, and the reactivity is slightly lower. For the higher alkanes, this difference diminishes and the rate constant per methylene group approaches a constant value of about 1.2E-12. The pre-exponential factor per methylene group is in the range of about (5-6)E-12 cm<sup>3</sup>/molec.-s., and the overall E/R decreases monotonically from about 600 K to 421 K.

Table 6 shows the analogous methylene contributions in the cycloalkanes, and we note that the rate constant per methylene group approaches essentially the same value as was seen in the alkane case, as the ring size increases. Similarly, the pre-exponential factors and E/R values (per CH<sub>2</sub>) for the higher cycloalkanes are nearly the same as those for the alkanes. The diminished reactivity of methylene groups seen in cyclopropane, due to increased C-H bond energies in that molecule, is largely but not entirely gone in cyclobutane. The lower reactivity of cyclopropane is due in part to a lower pre-exponential factor, following the general dependence of A-factors on rate constant that is observed in a large number of OH abstraction reactions.<sup>7</sup>

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Table 1. Experimental results for the rate constant ratios.

T(K)	Ratio	T(K)	Ratio	T(K)	Ratio	T(K)	Ratio
Ethane vs Propane		Butane vs Propane		Pentane vs Propane		Pentane vs Butane	
227	0.1576	293	2.133	308	3.189	298	1.570
237	0.1670	298	2.142	345	2.942	326	1.520
246	0.1773	328	1.985			351	1.500
265	0.1968	336	2.057			363.5	1.500
273	0.2038	358	1.950				
283	0.2134	361	1.966				
287	0.2162						
298	0.2276						
323	0.2452						
343	0.2692						
349	0.2687						
383	0.3035						
428	0.3372						
Hexane vs Propane		Hexane vs Butane		Cyclopropane vs Ethane		Cyclobutane vs Propane	
292	4.860	294	2.165	298	0.299		
298	4.696	310	2.116	276	0.289		
307	4.665	329	2.041	300	0.301		
315	4.618	354	2.023	316	0.310		
321	4.417	367	1.988	348	0.325		
337	4.300			363	0.337		
339	4.064	Hexane vs Pentane		383	0.333		
353	4.247			403	0.346		
357	4.045	303	1.387	421	0.353		
366	4.236						

Table 1 Continued. Experimental Results for Rate Constant Ratios

T(K)	Ratio	T(K)	Ratio	T(K)	Ratio	T(K)	Ratio
Cyclopentane vs Butane		Cyclopentane vs Hexane		Cyclohexane vs Propane		Cyclohexane vs Butane	
273	2.119	277	0.933	301	5.946	298	2.862
292	2.054	318	0.963	301	5.888	326	2.846
310	1.953	338	0.972			350	2.765
326	1.915	360	0.956			363	2.733
348	1.972						
354	1.913						
373	1.916						
398	1.910						
423	1.855						
Cyclohexane vs Pentane		Dimethyl ether vs Butane		Dimethyl ether vs Pentane		Cyclohexane vs Dimethyl ether	
298	1.798	293	1.180	295	0.811	306	2.261
312	1.816	298	1.151	305	0.824	324	2.309
338	1.786	313	1.187	318	0.754	351	2.342
368	1.765	333	1.140	328	0.778	361	2.299
		351	1.096	336	0.838		
				345	0.764		
				364	0.750		

Table 2. Derived Rate Constants for Alkanes and Comparison with Recent Work

Compound	A-factor*	E/R**	k(298 K)	Reference
Ethane	1.00E-11	1094	2.54E-13	Atkinson <sup>2</sup>
Propane	(1.29 ± 0.03)E-11	730 ± 6	1.11E-12	This work***
	1.03E-11	660	1.12E-12	Talukdar et al. <sup>23</sup>
	1.12E-11	693	1.09E-12	Donahue et al. <sup>10</sup>
	1.02E-11	657	1.12E-12	Atkinson <sup>2</sup>
n-Butane	(1.71 ± 0.15)E-11	590 ± 28	2.36E-12	This work***
	1.34E-11	503	2.48E-12	Talukdar et al. <sup>23</sup>
	1.34E-11	514	2.39E-12	Donahue et al. <sup>10</sup>
	1.11E-11	451	2.44E-12	Atkinson <sup>2</sup>
n-Pentane	(2.07 ± 0.14)E-11	515 ± 23	3.67E-12	This work***
	1.92E-11	454	4.18E-12	Talukdar et al. <sup>23</sup>
	2.97E-11	609	3.85E-12	Donahue et al. <sup>10</sup>
	1.60E-11	413	4.00E-12	Atkinson <sup>2</sup>
n-Hexane	(2.39 ± 0.09)E-11	462 ± 12	5.08E-12	This work***
	1.96E-11	384	5.40E-12	Donahue et al. <sup>10</sup>
	1.00E-11	182	5.43E-12	Atkinson <sup>2</sup>

\* Units are cm<sup>3</sup>/molec.-s.

\*\* Units K.

\*\*\* Errors shown are standard deviations of the least squares fit, and do not reflect uncertainties in the reference rate constant.

Table 3. Derived Rate Constants for Cycloalkanes and Comparison with Recent Work

Compound	A-factor*	E/R**	k(298 K)	Reference
Cyclopropane	$(5.15 \pm 0.14)\text{E-12}$	$1254 \pm 9$	7.65E-14	This work****
	1.63E-12	949	6.75E-14	Donahue <sup>9</sup>
	3.96E-12	1089	1.02E-13	Dobe et al. <sup>8</sup>
Cyclobutane	$(1.62 \pm 0.1)\text{E-11}$	$611 \pm 18$	2.09E-12	This work****
	1.17E-11	561	1.77E-12	Dobe et al. <sup>8</sup>
Cyclopentane	$(2.57 \pm 0.1)\text{E-11}$	$501 \pm 12$	4.79E-12	This work****
	2.40E-11	460	5.13E-12	Droege & Tully <sup>11</sup>
	1.88E-11	352	5.77E-12	Donahue et al. <sup>10</sup>
			5.18E-12	Jolly et al. <sup>15</sup>
Cyclohexane	$(3.71 \pm 0.29)\text{E-11}$	$511 \pm 25$	6.68E-12	This work****
	2.83E-11	408	7.20E-12	Donahue et al. <sup>10</sup>
	2.98E-11	423	7.21E-12	Droege & Tully <sup>11</sup>
	-	-	6.8E-12***	Sommerlade et al. <sup>22</sup>
	-	-	6.7E-12	Saunders et al. <sup>21</sup>
	1.89E-11	287	7.21E-12	Atkinson <sup>2</sup>

\* Units are  $\text{cm}^3/\text{molec.}\cdot\text{s}$ .

\*\* Units K.

\*\*\* Relative to n-hexane, using our k from Table 3

\*\*\*\* Errors shown are standard deviations of the fit, and do not reflect uncertainties in the reference rate constant.

Table 4. Results for Dimethyl Ether and Comparison with Recent Work

A-factor*	E/R**	k(298 K)	Reference
$(1.44 \pm 0.2) \text{E-11}$	$481 \pm 45$	2.88E-12	This work
7.1E-12	315	2.47E-12	Wallington et al. <sup>25</sup>
8.6E-12	318	2.95E-12	Arif et al. <sup>1</sup>
1.04E-11	373	2.98E-12	Tully and Droege <sup>24</sup>
-	-	2.35E-12	Nelson et al. <sup>19</sup>
-	-	2.86E-12***	Nelson et al. <sup>19</sup>

\* Units are  $\text{cm}^3/\text{molec.-s.}$

\*\* Units K.

\*\*\*Relative to cyclohexane, using our k from Table 3

Table 5. Contributions Per Methylene Group to the Overall Rate Constant and A-Factor in n-Alkanes, and the Effective Activation Temperature.<sup>a</sup>

(CH <sub>2</sub> ) <sub>n</sub>	k per CH <sub>2</sub> Group (cm <sup>3</sup> /molec-s.)	A-Factor per CH <sub>2</sub> Group (cm <sup>3</sup> /molec-s.)	E/R (K)
-CH <sub>2</sub> -	8.57E-12	6.52E-12	605
-CH <sub>2</sub> CH <sub>2</sub> -	1.05E-12	5.96E-12	517
-CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> -	1.14E-12	5.38E-12	462
-CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> -	1.20E-12	4.94E-12	421

a. See text for method of calculation of these quantities.

Table 6. Contributions Per Methylene Group to the Overall Rate Constant and A-Factor in Cycloalkanes, and the Overall Activation Temperature.

Compound	k per CH <sub>2</sub> Group (cm <sup>3</sup> /molec-s.)	A-Factor per CH <sub>2</sub> Group (cm <sup>3</sup> /molec-s.)	E/R (K)
Cyclopropane	2.55E-14	1.72E-12	1254
Cyclobutane	5.22E-13	4.06E-12	611
Cyclopentane	9.59E-13	5.15E-12	501
Cyclohexane	1.11E-12	6.18E-12	511

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### **Figure Captions**

**Fig. 1: Rate Constant Data for Propane.**

**Fig. 2: Rate Constant Data for Butane.**

**Fig. 3: Rate Constant Data for Pentane.**

**Fig. 4: Rate Constant Data for Hexane.**

**Fig. 5: Rate Constant Data for Cyclopropane.**

**Fig. 6: Rate Constant Data for Cyclopentane.**

**Fig. 7: Rate Constant Data for Cyclohexane.**

**Fig. 8: Rate Constant Data for Dimethyl ether.**

Figure 1

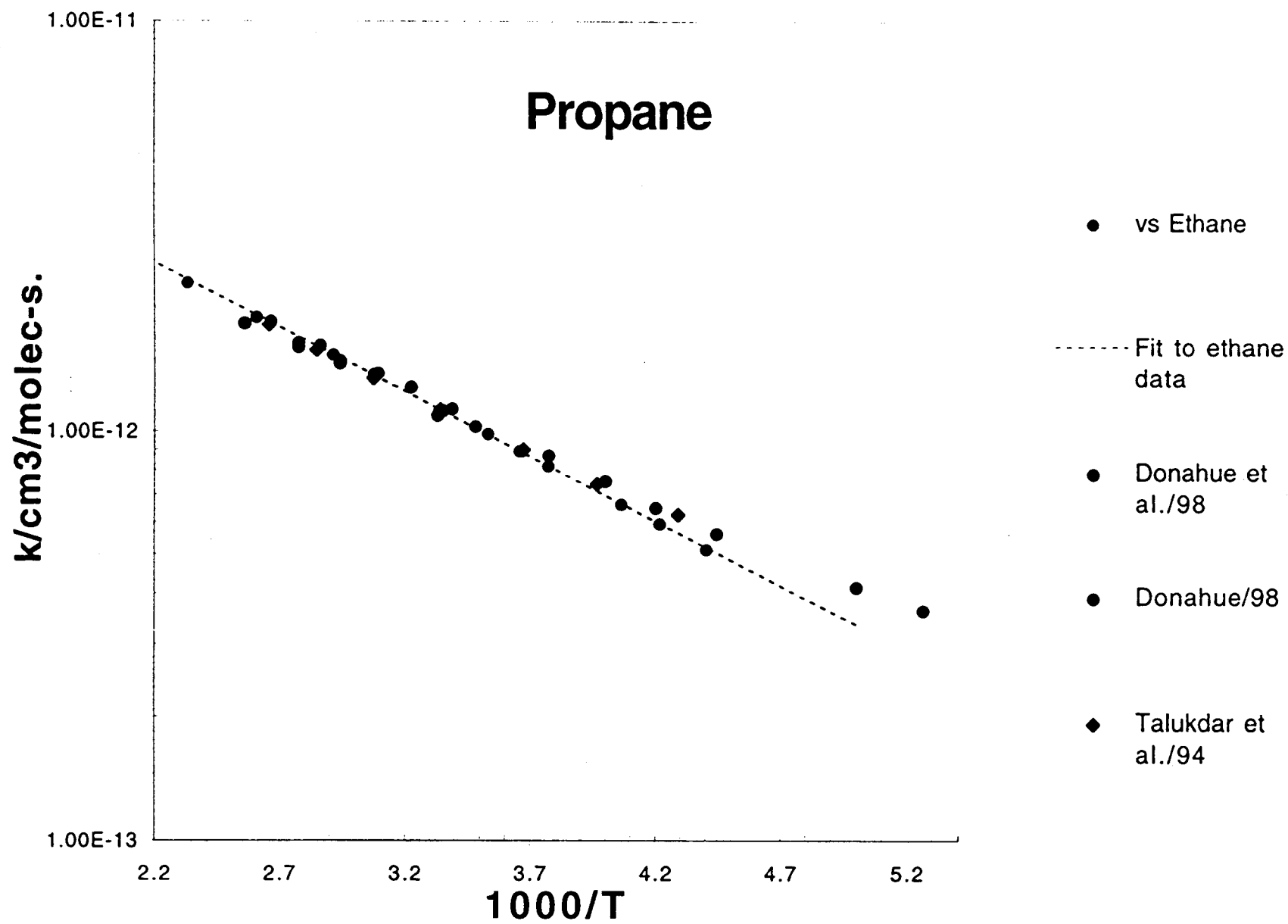


Figure 2

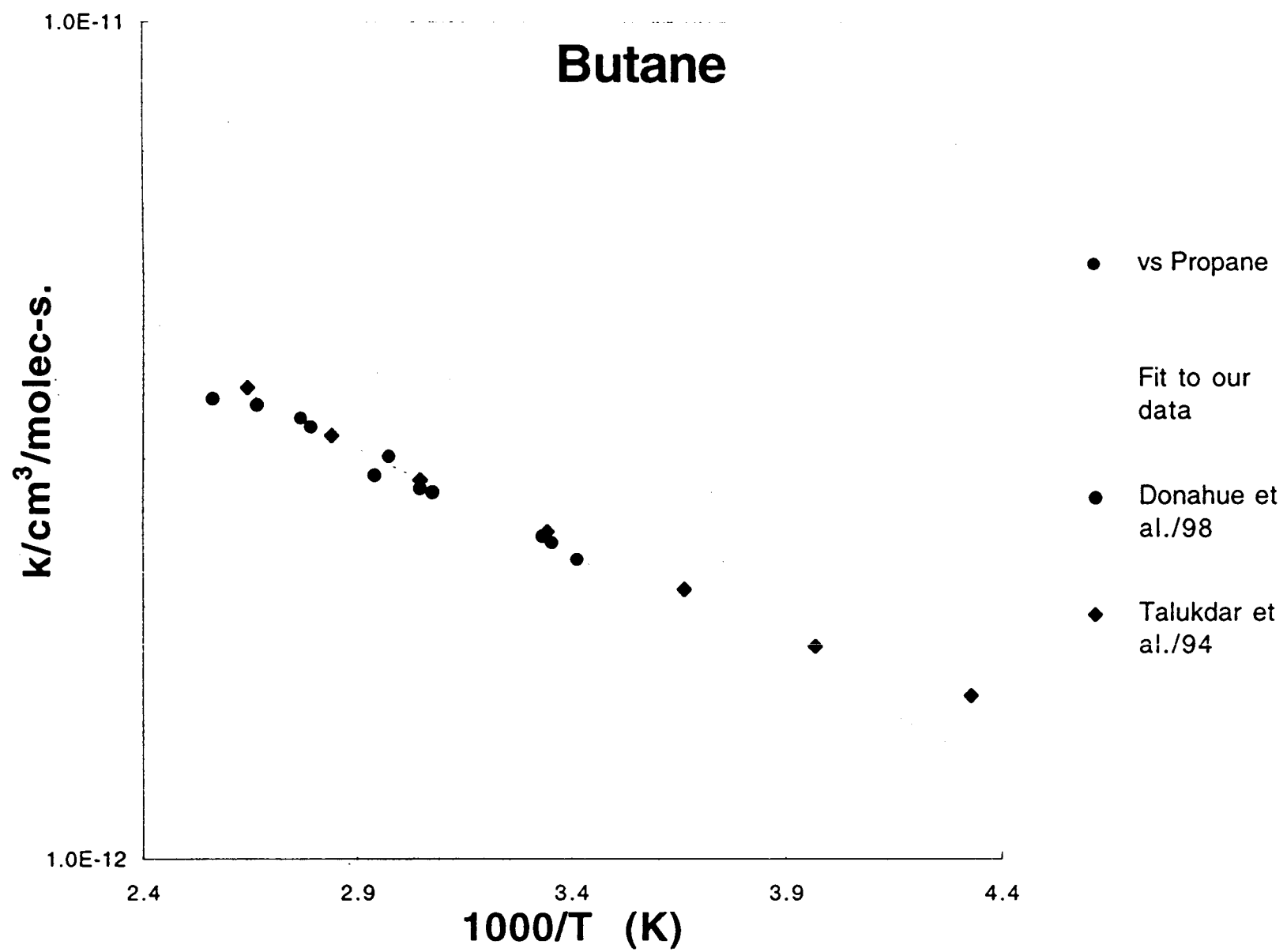


Figure 3

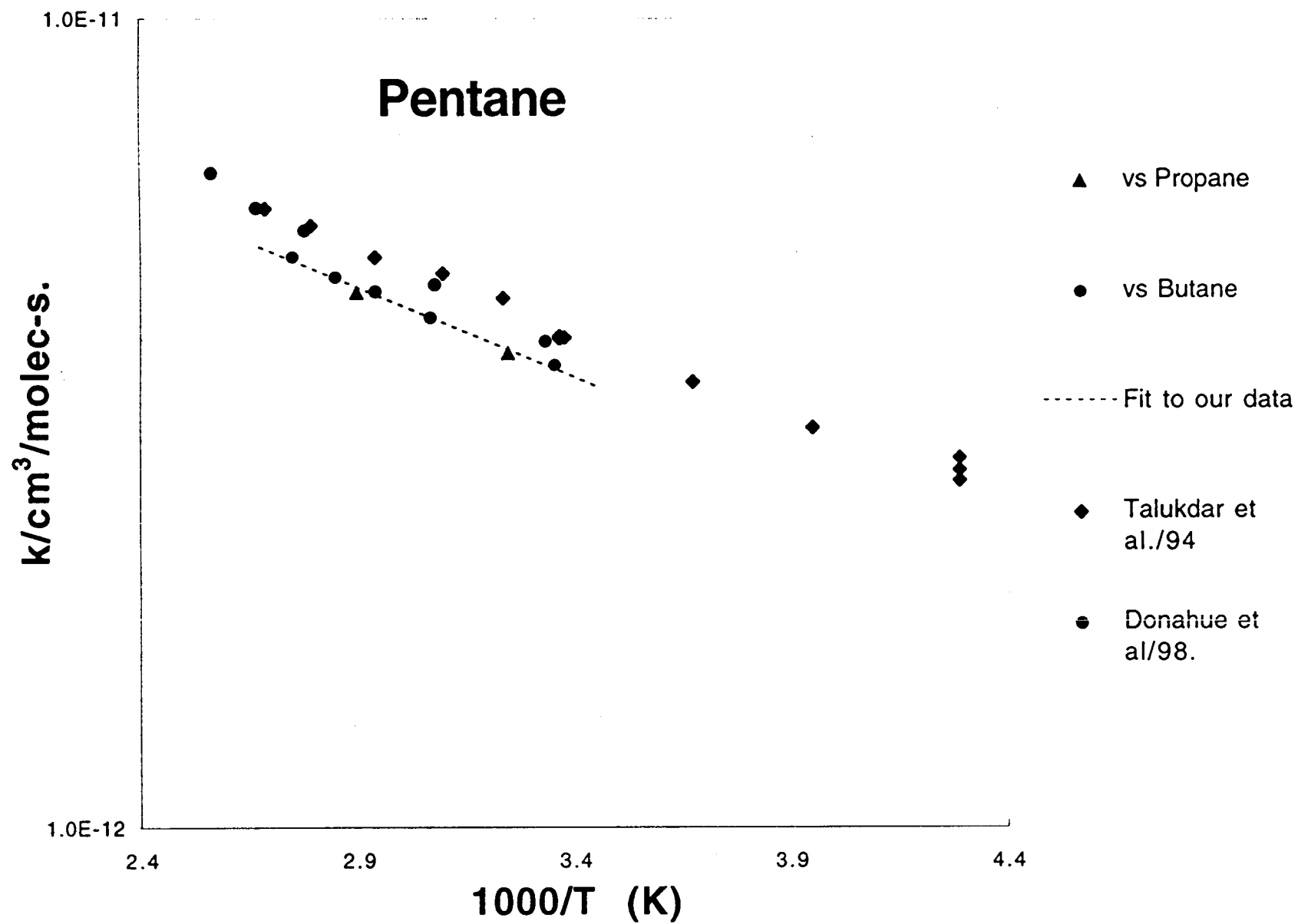


Figure 4

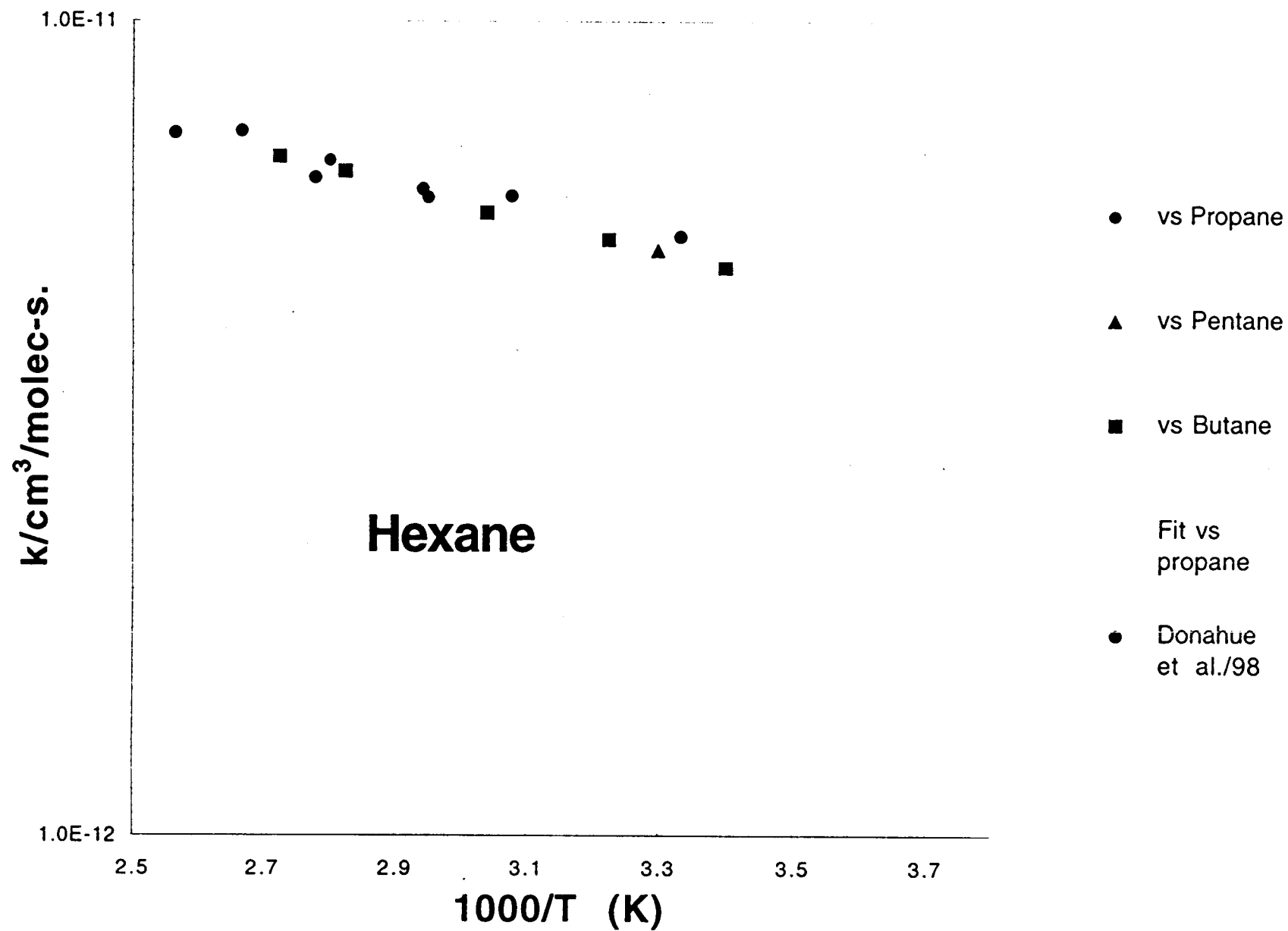


Figure 5

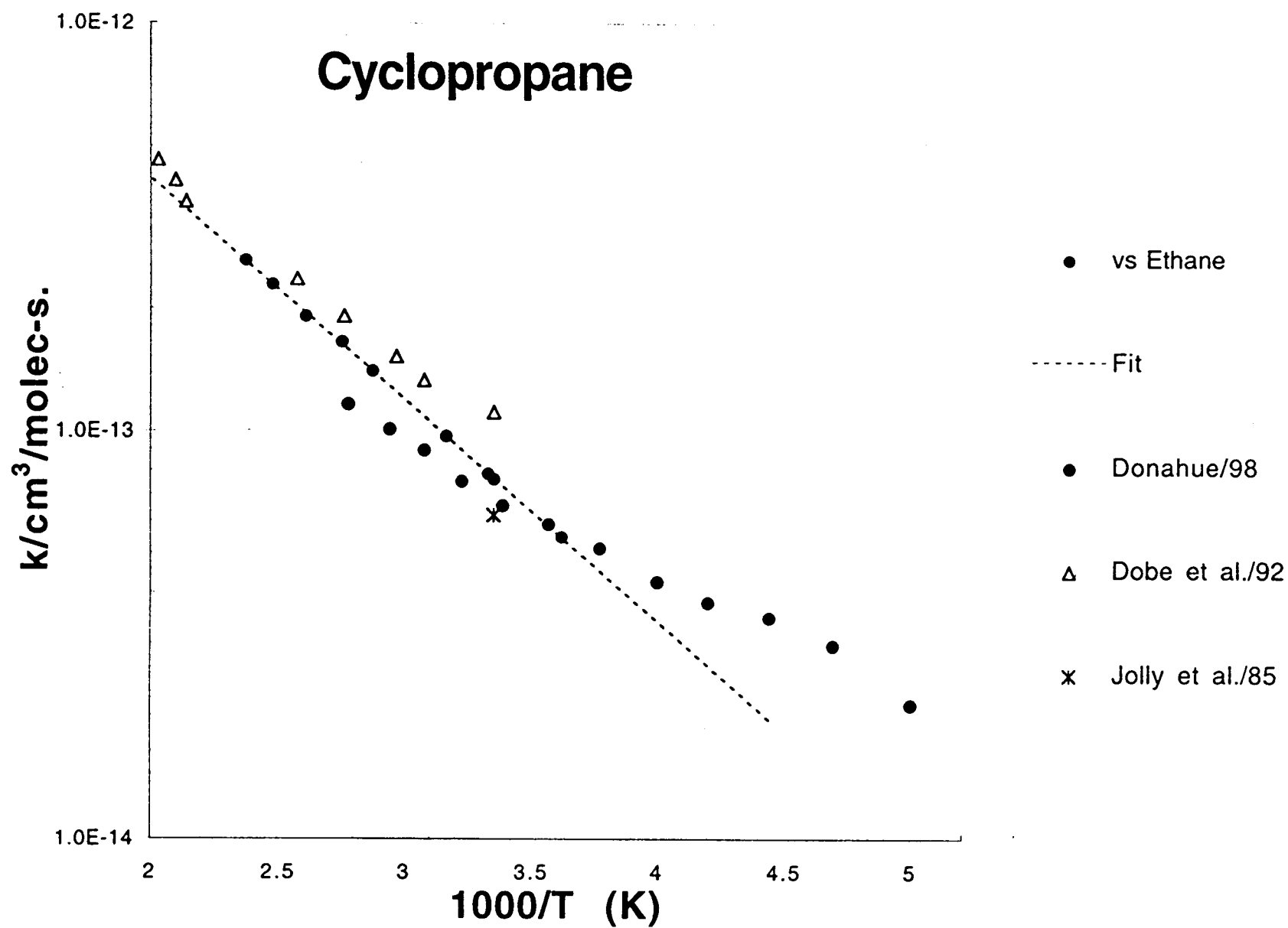


Figure 6

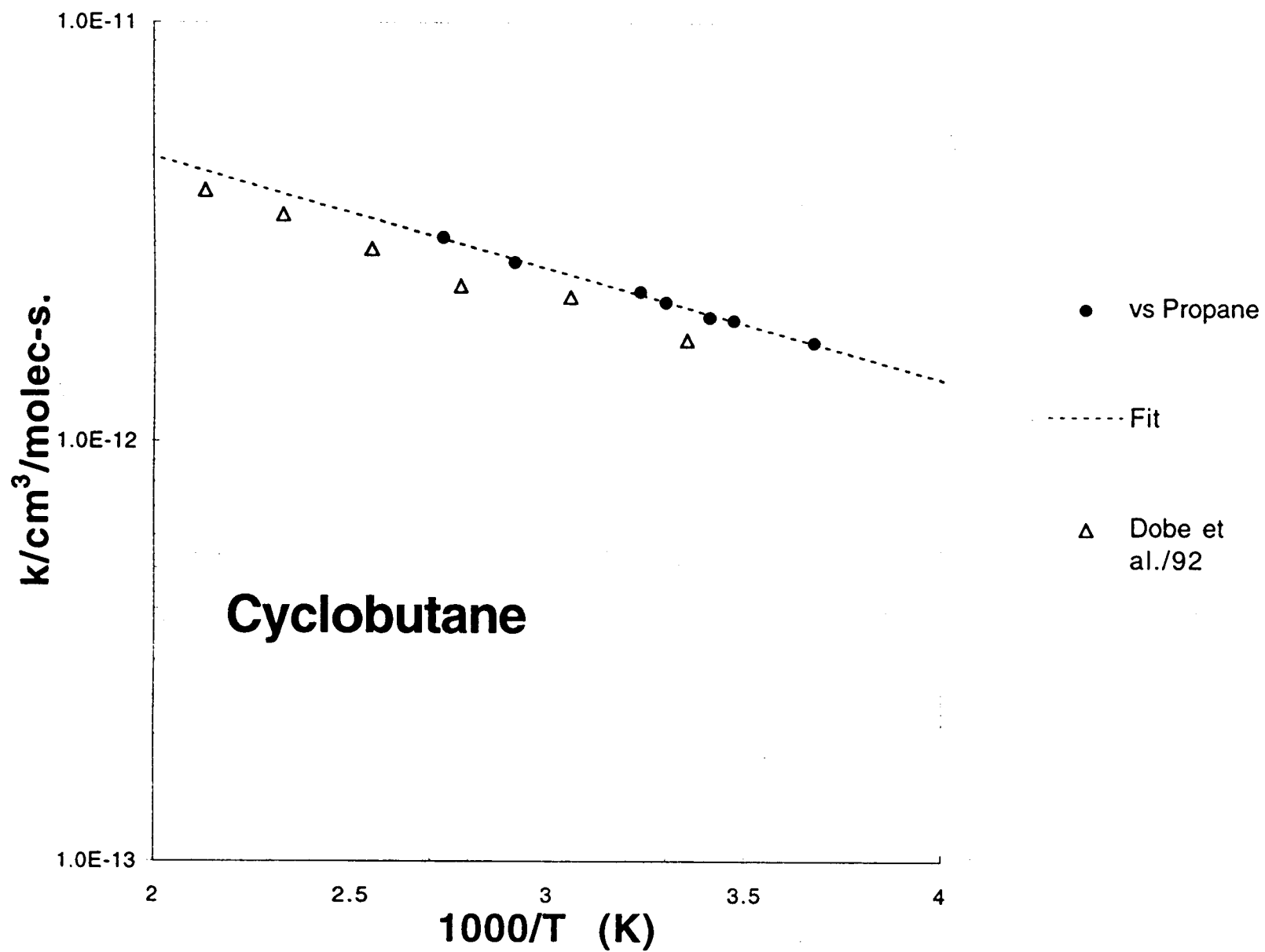


Figure 7

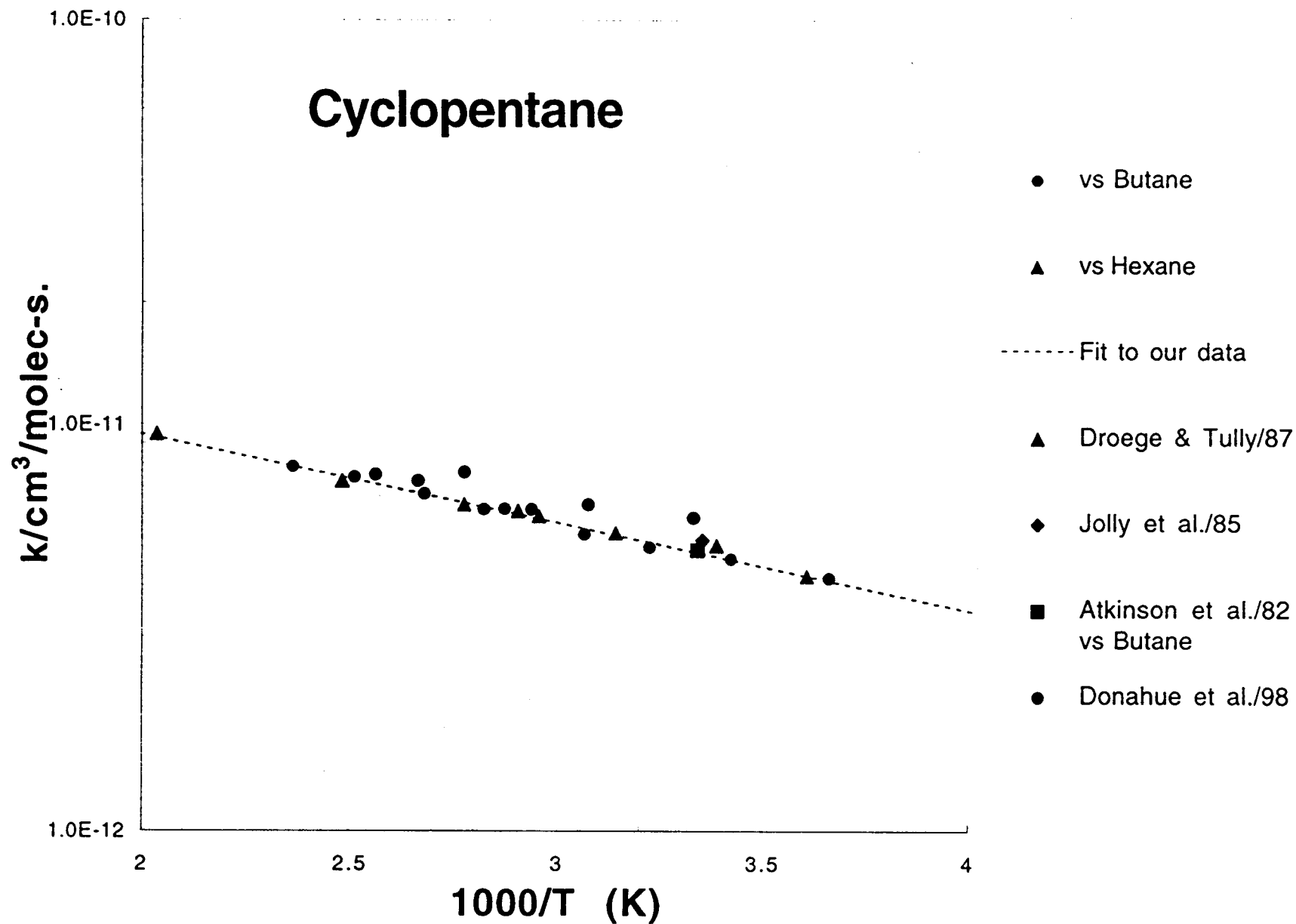


Figure 8

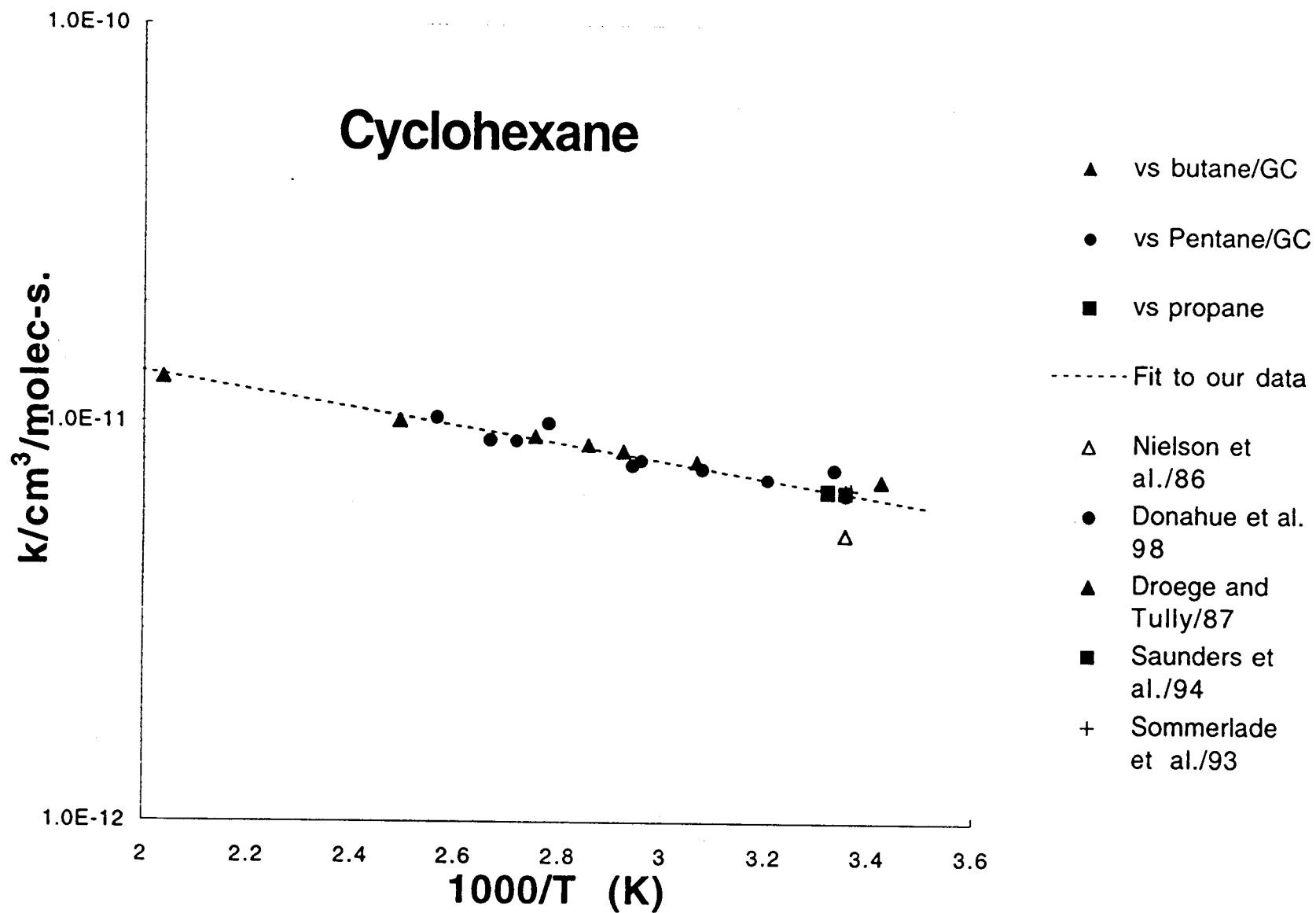


Figure 9

